Statistics and Nosé formalism for Ehrenfest dynamics

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Abstract. Quantum dynamics (i.e., the Schrödinger equation) and classical dynamics (i.e., Hamilton equations) can both be formulated in equal geometric terms: a Poisson bracket defined on a manifold. In this paper we first show that the hybrid quantum-classical dynamics prescribed by the Ehrenfest equations can also be formulated within this general framework, what has been used in the literature to construct propagation schemes for Ehrenfest dynamics. Then, the existence of a well defined Poisson bracket allows to arrive to a Liouville equation for a statistical ensemble of Ehrenfest systems. The study of a generic toy model shows that the evolution produced by Ehrenfest dynamics is ergodic and therefore the only constants of motion are functions of the Hamiltonian. The emergence of the canonical ensemble characterized by the Boltzmann distribution follows after an appropriate application of the principle of equal a priori probabilities to this case. Once we know the canonical distribution of a Ehrenfest system, it is straightforward to extend the formalism of Nosé (invented to do constant temperature Molecular Dynamics by a non-stochastic method) to our Ehrenfest formalism. This work also provides the basis for extending stochastic methods to Ehrenfest dynamics.

1. Introduction

The Schrödinger equation for a combined system of electrons and nuclei enables us to predict most of the chemistry and molecular physics that surrounds us, including bio-physical processes of great complexity. Unfortunately, this task is not possible in general, and approximations need to be made; one of the most important and successful being the classical approximation for a number of the particles. Mixed quantum-classical dynamical (MQCD) models are therefore necessary and widely used.

The so-called "Ehrenfest equations" (EE) result from a straightforward application of the classical limit to a portion of the particles of a full quantum system, and constitute the most evident MQCD model, as well as a first step in the intricated problem of mixing quantum and classical dynamics. For example, it can be noted that much of the field of molecular dynamics (MD) –whether ab initio or not– is based on equations that can be obtained from further approximations to the Ehrenfest model: for instance, written in the adiabatic basis, the Ehrenfest dynamics collapse into Born-Oppenheimer MD if we assume the non-adiabatic couplings to be negligible.

It is not the purpose of this work, however, to dwell into the justification or validity conditions of the EE (see for example Refs. [1, 2, 3, 4, 5] for rigurous analyses). Nor is it to investigate the unsettled problem of which is the best manner of mixing quantum and classical degrees of freedom. The Ehrenfest model has a proven application niche, and for this reason we are interested in investigating some of its theoretical foundations, in a manner and with an aim that we describe in the following. For recent progress in non-adiabatic electronic dynamics in MQCD see, for example, Ref. [6]

Classical mechanics (CM) can be formulated in several mathematical frameworks, each corresponding to a different level of abstraction (Newton equations, the Hamiltonian formalism, the Poisson brackets, etc.). Perhaps its more abstract and general formulation is geometrical, in terms of Poisson manifolds. Similarly, quantum mechanics (QM) can be formulated in different ways, some of which resemble its classical counterpart. For example, the observables (self-adjoint linear operators) are endowed with a Poisson algebra almost equal to the one that characterizes the dynamical variables in CM. Moreover, Schrödinger equation can be recast into Hamiltonian equations form (see [7]) by transforming the complex Hilbert space into a real one of double dimension; the observables are also transformed into dynamical functions in this new phase space, in analogy with the classical case. Finally, a Poisson bracket formulation has also been established for QM, which permits to classify both the classical and the quantum dynamics under the same heading.

This variety of formulations does not emerge from academic caprice; the successive abstractions simplify further developments of the theory, such as the step from microscopic dynamics to statistical dynamics: the derivation of Liouville equation (or von Neumann equation in the quantum case), at the heart of statistical dynamics, is based on the properties of the Poisson algebra.

The issue regarding what is the correct equilibrium distribution of a mixed

quantum-classical system is seen as a very relevant one [8, 9, 10, 11, 12, 13, 14, 15, 16]. An attempt to its derivation can be found in Ref. [14], where they arrive to the same distribution that we will advocate below, although it is found using the Nosé-Hoover technique [17, 18], which in principle is only a mathematical scheme to produce the equilibrium, and which the very authors of Ref. [14] agree that it is not clear how to apply to a mixed quantum-classical dynamics. On the other hand, in Ref. [8] they provide some analytical results about this distribution, but not in the case in which the system of interest is described by the EE; instead (and as in Refs. [9, 10]), they assume that the system is fully quantum, and that it is coupled to an infinite classical bath via an Ehrenfest-like interaction.

It is therefore necessary to base Ehrenfest dynamics –or any other MQCD model– on firm theoretical ground. In particular, we are interested in establishing a clear path to statistical mechanics for Ehrenfest systems, which in our opinion should be done by first embedding this dynamics into the same theoretical framework used in the pure classical or quantum cases (i.e., Poisson brackets, symplectic forms, etc). Then the study of their statistics will follow the usual steps for purely classical or purely quantum ensembles. In this respect, it should be noted that other approaches to MQCD (not based on Ehrenfest equations) exist [19, 20, 21], and to their corresponding statistics [22, 23], however it has been found that the formulation of well defined quantum-classical brackets (i.e., satisfying the Jacobi identity and Leibniz derivation rule) is a difficult issue [24, 25, 26, 27]. On the contrary, as shown below, and as a result of the fact that the evolution of a quantum system can be formulated in terms of Hamilton equations similar to those of a classical system [4, 28], we will not have difficulties in a rigorous formulation of the Ehrenfest dynamics in terms of Poisson brackets.

The roadmap of this project is the following: In Section 2 we recall the definition of the Ehrenfest model. In Section 3 we quickly summarize the formulation of CM in terms of Poisson brackets. Then we summarize, in Section 4, the analogous description of QM in terms of geometrical objects which can be found, for example, in Refs. [29, 7, 30, 31, 32, 33, 34, 35, 36]. These works demonstrate how Schrödinger equation can be written as a set of (apparently classical) Hamiltonian equations. Also, by using a suitable definition of observables as functions on the (real) set of physical states, Schrödinger equation can be written in terms of a canonical Poisson bracket. QM appears in this way as "classical", although the existence of extra algebraic structure encodes the probabilistic interpretation of measurements, and the superposition and indetermination principles [29, 30, 31, 32, 33]. As we have in mind the application to computer simulations, we will consider only finite dimensional quantum systems, obtained by a suitable sample of the electronic states. This simplifies significantly the description, even if the framework is valid also for the infinite dimensional case (see [33]).

For the case of Ehrenfest dynamics, we can now combine it (Section 5) with CM, whose Poisson bracket formulation is very well known. This is the first of the contributions of the paper: once we realize that the geometric description of classical

and quantum dynamics are formally analogous, we can combine them as we do when combining different classical systems. The procedure is very simple: we consider as a global phase space the Cartesian product of the electronic and the nuclear phase spaces and define a global Poisson bracket simply as the sum of the classical and the quantum ones. It is completely straightforward to prove that such a Poisson bracket is well defined and that it provides the correct dynamical equations (EE). From a formal point of view, the resulting dynamics is more similar to a classical system than to a quantum one, although when considering a pure quantum system the dynamics is the usual Schrödinger one. This is not surprising since the coupling of the classical and quantum systems makes the total system nonlinear in its evolution, and this is one of the most remarkable differences between a classical and a quantum system in any formulation.

Once the dynamical description as a Poisson system is at our disposal, it is a very simple task (Section 6) to construct the corresponding statistical description following the lines of Refs. [37] and [38]. This is another main result of the paper: not having proved the Hamiltonian nature of Ehrenfest dynamics, it was not possible to provide a self-consistent definition of the Statistics corresponding to it. Once the Hamiltonian description is available, the definition of this Statistics is straightforward.

The formal similarity with the CM case ensures the correctness of the procedure and allows us to derive a Liouville equation. The choice of the equilibrium distribution is based, as usual, in the principle of equal *a priori* probablities implicitely used by Gibbs and clearly formulated by Tolman [39]. After this, in Section 7 we extend Nosé formalism to the Ehrenfest MQCD framework and provide then a method to simulate the canonical ensemble of Ehrenfest systems. This is the final main contribution of the paper.

Please note that for systems where the Born-Oppenheimer approximation is not sufficient, the use of the canonical ensemble of a mixed quantum-classical system such as Ehrenfest's is compulsory, since those systems where the electronic gap is small can be affected by electronic temperature effects of the same order. Therefore, a simple mechanism of simulation such as Nosé is very important for practical applications.

Finally, in the conclusions (Section 8), we propose to extend, within our formalism, stochastic methods to Ehrenfest dynamics.

2. The Ehrenfest model

The Ehrenfest Equations have the following general form:

$$\dot{\vec{R}}_J(t) \quad = \langle\psi(t)|\frac{\partial \hat{H}}{\partial \vec{P}_J}(\vec{R}(t), \vec{P}(t), t)|\psi(t)\rangle, \tag{1}$$

$$\dot{\vec{P}}_J(t) \quad = -\langle\psi(t)|\frac{\partial \hat{H}}{\partial \vec{R}_J}(\vec{R}(t), \vec{P}(t), t)|\psi(t)\rangle, \tag{2}$$

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle = \hat{H}(\vec{R}(t), \vec{P}(t), t)|\psi(t)\rangle, \tag{3}$$

where $(\vec{R}, \vec{P})$ denote collectively the set of canonical position and momenta coordinates of a set of classical particles, whereas ψ is the wavefunction of the quantum part of the system (see Ref [40] for the issue of the Hellmann-Feynman theorem in this context, i.e., whether one should take the derivative inside or outside the expectation value).

This and other MQCD models appear in different contexts; in many situations, the division into quantum and classical particles is made after the electrons have been integrated out, and is used to *quantize* a few of the nuclear degrees of freedom. However, a very obvious case to use EE is when we want to treat electrons quantum mechanically, and nuclei classically. In order to fix ideas, let us use this case as an example: the Hamiltonian for the full quantum system is:

$$
\begin{aligned}
\hat{H} := & -\hbar^2 \sum_J \frac{1}{2M_J} \nabla_J^2 - \hbar^2 \sum_j \frac{1}{2} \nabla_j^2 + \frac{1}{4\pi\epsilon_0} \sum_{J<K} \frac{Z_J Z_K}{|\vec{R}_J - \vec{R}_K|} \\
& - \frac{1}{4\pi\epsilon_0} \sum_{j<k} \frac{1}{|\vec{r}_j - \vec{r}_k|} - \frac{1}{4\pi\epsilon_0} \sum_{J,j} \frac{Z_J}{|\vec{R}_J - \vec{r}_j|} \\
=: & -\hbar^2 \sum_J \frac{1}{2M_J} \nabla_J^2 - \hbar^2 \sum_j \frac{1}{2} \nabla_j^2 + V_{n-e}(\vec{r}, \vec{R}) \\
=: & -\hbar^2 \sum_J \frac{1}{2M_J} \nabla_J^2 + H_e(\vec{r}, \vec{R}),
\end{aligned}
\tag{4}
$$

where all sums must be understood as running over the whole natural set for each index. M_J is the mass of the J-th nucleus in units of the electron mass, and Z_J is the charge of the J-th nucleus in units of (minus) the electron charge. Also note that we have defined the nuclei-electrons potential $V_{n-e}(\vec{r}, \vec{R})$ and the electronic Hamiltonian $H_e(\vec{r}, \vec{R})$ operators.

The EE may then be reached in the following way [1, 2, 3, 4, 5]: first, the full wave function is split into a product of nuclear and electronic wave functions, which leads to the time dependent self-consistent field model, in which the two subsystems are quantum and coupled. Afterwards, a classical limit procedure is applied to the nuclear subsystem, and the EE emerge naturally. In terms of the nuclei positions $\vec{R}_J$ and of the element of the Hilbert space $|\psi\rangle \in \mathcal{H}$ which encodes the state of the electrons of the system, the Ehrenfest dynamics is then given by

$$
M_J \ddot{\vec{R}}_J = -\langle \psi | \nabla_J H_e(\vec{r}, \vec{R}) | \psi \rangle, \tag{5}
$$

$$
i\hbar \frac{d}{dt} |\psi\rangle = H_e(\vec{r}, \vec{R}) |\psi\rangle. \tag{6}
$$

These equations can be given a Hamiltonian-type description by introducing a Hamiltonian function of the form:

$$
H(\vec{R}, \vec{P}) = \sum_J \frac{\vec{P}_J^2}{2M_J} + \langle \psi | H_e(\vec{r}, \vec{R}) | \psi \rangle. \tag{7}
$$

Then, by fixing a relation of the form $\vec{P}_J = M\dot{\vec{R}}_J$, we obtain a structure similar to

Hamilton equations:

$$\dot{\vec{R}}_J = \frac{\vec{P}_J}{M_J}, \tag{8}$$

$$\dot{\vec{P}}_J = -\langle \psi | \nabla_J H_e(\vec{r}, \vec{R}) | \psi \rangle, \tag{9}$$

$$i\hbar \frac{d}{dt} |\psi\rangle = H_e(\vec{r}, \vec{R}) |\psi\rangle. \tag{10}$$

This set of equations perhaps constitutes the most evident MQCD model, as well as a first step in the intricated problem of mixing quantum and classical dynamics. In this sense, it is interesting to note that written in the adiabatic basis $\{\psi_m(\vec{R})\}_m$ formed by the eigenvectors of the electronic Hamiltonian,

$$\hat{H}_e(\vec{r}, \vec{R}) |\psi_m(\vec{R})\rangle = E_m(\vec{R}) |\psi_m(\vec{R})\rangle, \tag{11}$$

the Ehrenfest dynamics collapse into ground state Born-Oppenheimer MD (gsBOMD) if we assume the non-adiabatic couplings to be negligible. Indeed, by expanding the wave function in this basis (some relevant considerations related to this change of variables can be found in Ref. [40], Section 2 "Ehrenfest Dynamics: Fundaments and implications for First Principles Simulations"),

$$|\psi(t)\rangle = \sum_m c_m(t) |\psi_m(\vec{R}(t))\rangle. \tag{12}$$

the equations are transformed into:

$$M_J \ddot{\vec{R}}_J(t) = -\sum_m |c_m(t)|^2 \nabla_J E_m(\vec{R}(t))$$
$$- \sum_{mn} c_m^*(t) c_n(t) \left[E_m(\vec{R}(t)) - E_n(\vec{R}(t)) \right] \vec{d}_J^{mn}(\vec{R}(t)). \tag{13}$$

$$i \frac{\mathrm{d}}{\mathrm{d}t} c_m(t) = E_m(\vec{R}(t)) c_m(t) - i \sum_n c_n(t) \left[\sum_J \dot{\vec{R}}_J \cdot \vec{d}_J^{mn}(\vec{R}(t)) \right] \tag{14}$$

where the "non-adiabatic couplings" are defined as:

$$\vec{d}_J^{mn}(\vec{R}) := \langle \psi_m(\vec{R}) | \nabla_J \psi_n(\vec{R}) \rangle. \tag{15}$$

If these are negligible, and we assume that the electronic system starts from the ground state ($c_m(0) = \delta_{m0}$), the EE model reduces to gsBOMD:

$$M_J \ddot{\vec{R}}_J(t) = \nabla_J E_0(\vec{R}(t)), \tag{16}$$

$$c_m(t) = \delta_{m0}. \tag{17}$$

In spite of the formal similarities, the EE equations do not correspond yet to Hamilton equations, since they lack a global phase space formulation (encompassing both the nuclear and the electronic degrees of freedom) and a Poisson bracket.

3. Classical mechanics in terms of Poisson brackets

We begin by recalling very quickly the Hamiltonian formulation of classical dynamics (we address the interested reader to a classical text, such as Ref. [41], for a detailed presentation). Let us consider a classical system with phase space M_C, which, for the sake of simplicity, we can identify with $\mathbb{R}^{2n}$, where n is the number of degrees of freedom (strictly speaking, M_C is a general $2n$-dimensional manifold, homeomorphic to $\mathbb{R}^{2n}$ only locally). The $2n$ dimensions correspond with the n position coordinates that specify the configuration of the system, and the n corresponding momenta (mathematically, however, the division into "position" and "momenta" coordinates is a consequence of Darboux theorem – see below).

The "observables" in classical mechanics are differentiable functions

$$f : M_C \to \mathbb{R}, \tag{18}$$

that assign the result of a measurement to every point in M_C. On this set of functions $C^\infty(M_C)$ we introduce the **Poisson bracket**, $\{\cdot, \cdot\}$, a bilinear operation

$$\{\cdot, \cdot\} : C^\infty(M_C) \times C^\infty(M_C) \to C^\infty(M_C), \tag{19}$$

which:

- is antisymmetric,

$$\{f, g\} = -\{g, f\}, \qquad \forall f, g \in C^\infty(M_C),$$

- satisfies the Jacobi identity, i.e., $\forall f, g, h \in C^\infty(M_C)$:

$$\{f, \{g, h\}\} + \{h, \{f, g\}\} + \{g, \{h, f\}\} = 0,$$

- and satisfies the Leibniz rule ,i.e., $\forall f, g, h \in C^\infty(M_C)$:

$$\{f, gh\} = \{f, g\}h + g\{f, h\}.$$

If the Poisson bracket is non degenerate (it has no Casimir functions), a theorem due to Darboux ensures that there exists a set of coordinates $(\vec{R}, \vec{P})$ for which the bracket has the "standard" form (at least locally, in a neighbourhood of every point):

$$\{f_1, f_2\} = \sum_{k=1}^{n} \frac{\partial f_1}{\partial P_k} \frac{\partial f_2}{\partial R^k} - \frac{\partial f_1}{\partial R^k} \frac{\partial f_2}{\partial P_k}. \tag{20}$$

These coordinates are called Darboux coordinates. They are specially useful when studying the dynamics and invariant measures of a Hamiltonian system [41]. In the rest of the paper we shall be working with this kind of coordinates.

The Poisson bracket allows us to introduce the concept of Hamiltonian vector field: Given a function $f \in C^\infty(M_C)$ and a Poisson bracket $\{\cdot, \cdot\}$, a vector field, X_f, is said to be its **Hamiltonian vector field** if

$$X_f(g) = \{f, g\}, \qquad \forall g \in C^\infty(M_C).$$

In standard coordinates:

$$X_f = \sum_{k=1}^{n} \frac{\partial f(R,P)}{\partial P_k} \frac{\partial}{\partial R^k} - \frac{\partial f(R,P)}{\partial R^k} \frac{\partial}{\partial P_k}. \tag{21}$$

We shall call a **Hamiltonian system** to a triple $(M_C, \{\cdot,\cdot\}, H)$, where $\{\cdot,\cdot\}$ is a Poisson bracket on M_C, and $H \in C^\infty(M_C)$ is the Hamiltonian of the sytem. The dynamics of a Hamiltonian system can be formulated in two alternative manners:

- The trajectories of the system are given by the integral curves of the Hamiltonian vector field X_H.

- If we consider instead the set of classical observables, the dynamics is written as the Poisson bracket of the Hamiltonian function H with any other function, i.e.,

$$\frac{df}{dt} = \{H, f\}, \qquad \forall f \in C^\infty(M_C). \tag{22}$$

Both approaches are equivalent: the differential equations that determine the integral curves of the Hamiltonian vector field are given by Eq. (22), for the functions "position" and "momenta" of each particle (i.e., $\vec{R}$ and $\vec{P}$). These equations are nothing else but Hamilton equations:

$$\dot{R}^j = \frac{\partial H}{\partial P_j}, \tag{23}$$

$$\dot{P}_j = -\frac{\partial H}{\partial R^j}. \tag{24}$$

4. Summary of geometric quantum mechanics

The aim of this section is to provide a description of quantum mechanical systems by using the same geometric tools which are used to describe classical mechanical systems, outlined above. It is just a very quick summary of the framework which has been developed in the last 30 years and which can be found in Refs. [29, 7, 30, 31, 32, 33, 34, 35, 36] and references therein. For the sake of simplicity, we shall focus only on the finite dimensional case. The Hilbert space $\mathcal{H}$ becomes then isomorphic to $\mathbb{C}^n$ for n a natural number, $\mathbb{C}^n \sim \mathcal{H}$:

4.1. The states

Consider a basis $\{|\psi_k\rangle\}$ for $\mathcal{H}$. Each state $|\psi\rangle \in \mathcal{H}$ can be written in that basis with complex components $\{z_k\}$:

$$|\psi\rangle = \sum_k z_k |\psi_k\rangle.$$

We can just take the vector space inherent to the Hilbert space, and turn it into a real vector space M_Q, by splitting each coordinate in its real and imaginary part:

$$z_k = q_k + i p_k \mapsto (q_k, p_k) \in \mathbb{R}^{2n} \equiv M_Q.$$

We will use real coordinates (q_k, p_k), $k = 1, \ldots, n$ to represent the points of $\mathcal{H}$ when thought as real manifold elements. From this real point of view the similarities between the quantum dynamics and the classical one described in the previous section will be more evident. Sometimes it will be useful to maintain the complex notation ψ or z_k for the elements of the Hilbert space. Please notice that, despite the use of "q" and "p", these coordinates have in principle no relation at all, with the position or the momentum of the quantum system. They are simply the real and imaginary parts of the complex coordinates used to represent the (finite-dimensional) Hilbert space vector in the chosen basis. Therefore, the resulting geometrical description has no relation with the usual phase-space descriptions of Quantum Mechanics, such as the Wigner representation, which is defined for infinite-dimensional quantum systems and where the coordinates to represent the point of the phase space do correspond to the spectra of the position and momentum operators. For the same reason, there is no relation with any classical limit of the quantum system: the description in terms of these coordinates (q, p) is purely quantum.

There is no one-to-one correspondence between physical states and elements of the Hilbert space used to describe it; it is a well known fact that physical states are independent of global phases. This ambiguity also translates to the formulation with real vector spaces. Two equivalent states are related by a phase transformation; the best way to characterize these transformations in M_Q is by introducing their infinitesimal generator, given by:

$$\Gamma := \sum_k \left(q_k \frac{\partial}{\partial p_k} - p_k \frac{\partial}{\partial q_k} \right), \tag{25}$$

This is a vector field whose meaning is clear if we realize that a phase change modifies the angle of the complex number representing the state, when considered in polar form (i.e., in polar coordinates $\{r_k, \theta_k\}_{k=1,\cdots,n}$ with $z_k = r_k e^{i\theta_k}$, Eq. (25) becomes $\Gamma = \sum_k \partial_{\theta_k}$). Then, from a geometrical point of view we can use Eq. (25) in two ways:

- Computing its integral curves, which are the different states which are obtained from an initial one by a global phase multiplication.
- Acting with the vector field on functions of M_Q. A function will be acceptable as an observable if it is invariant under phase transformations, i.e., $\Gamma f = 0$.

In a quantum Hilbert space, we also consider two states to be equivalent if they merely differ by their norm. One may therefore only consider the sphere of states with norm equal to one in $\mathbb{C}^n$; this corresponds in the real-vector-space description to the $(2N_Q - 1)$–dimensional sphere:

$$S_Q := \left\{ (\vec{q}, \vec{p}) \in M_Q | \sum_k (q_k^2 + p_k^2) = 1 \right\}. \tag{26}$$

It is immediate that the vector field Γ is tangent to S_Q, since the phase change preserves the norm of the state.

4.2. The Poisson bracket

Taking as coordinates $z_k = q_k + ip_k$, the components of a vector in an orthonormal basis we can define a Poisson bracket in M_Q, by:

$$\{f,g\} := \sum_k \frac{1}{2}\left(\frac{\partial f}{\partial p_k}\frac{\partial g}{\partial q_k} - \frac{\partial f}{\partial q_k}\frac{\partial g}{\partial p_k}\right), \tag{27}$$

that corresponds to the standard Poisson bracket in classical mechanics. It will also be useful to introduce a symmetric bracket by

$$\{f,g\}_+ := \sum_k \frac{1}{2}\left(\frac{\partial f}{\partial q_k}\frac{\partial g}{\partial q_k} + \frac{\partial f}{\partial p_k}\frac{\partial g}{\partial p_k}\right). \tag{28}$$

We have made use of a specific basis; one may think that the definition of the brackets could depend on the choice of the basis. However, it is a matter of simple algebra to prove that this is not the case.

An important property of the brackets defined above is that they are preserved by the vector field Γ in Eq. (25) in the sense that

$$\Gamma\{f,g\} = \{\Gamma f, g\} + \{f, \Gamma g\}$$

and

$$\Gamma\{f,g\}_+ = \{\Gamma f, g\}_+ + \{f, \Gamma g\}_+.$$

A fact that can be proved with a simple computation. This property is important for us because it implies that the symmetric or antisymmetric bracket of two phase invariant functions will also be phase invariant:

$$\Gamma f = \Gamma g = 0 \Rightarrow \Gamma\{f,g\} = \Gamma\{f,g\}_+ = 0.$$

4.3. The observables

We now proceed to discuss how to represent the physical observables on this new setting. Instead of considering the observables as linear operators (plus the usual requirements, self-adjointness, boundedness, etc.) on the Hilbert space $\mathcal{H}$, we shall be representing them as functions defined on the real manifold M_Q, as it is done in classical mechanics. But we can not forget the linearity of the operators, and thus not any function is acceptable. We will consider, for any operator $A \in \mathrm{Lin}(\mathcal{H})$, the quadratic function

$$f_A(\psi) := \langle \psi | A\psi \rangle. \tag{29}$$

We shall denote the set of such functions as $\mathcal{F}_s(M_Q)$.

Notice that this definition of observable is different from the analogous one in the classical case. In the classical framework a state, represented by a point in M_C, provides a well defined result for any observable $f : M_C \to \mathbb{R}$. In this geometric quantum mechanics (GQM in the following) framework, on the other hand, the value at a given state of $f_A \in \mathcal{F}_s(M_Q)$ provides just the average value of the corresponding operator in

that state. Besides, contrarily to the classical case, not all the C^∞ functions on M_Q are regarded as observables, but only those of the form of (29).

Once the definition has been stated, one must verify that it is a consistent one, meaning that (i) they are phase invariant functions ($\Gamma f = 0$), and (ii) the set of observables is closed with respect to both the symmetric and antisymmetric brackets (i.e. the bracket of two elements of $\mathcal{F}_s(M_Q)$ is also an element of $\mathcal{F}_s(M_Q)$). Both facts can be proven by direct computation. The second proof, however, is interesting because it leads us to consider the relevant algebraic operations within $\mathcal{F}_s(M_Q)$. In the usual approach of quantum mechanics, there are three algebraic structures on the set of operators, which turn out to be meaningful and important for the physical description:

- The associative product of two operators:

$$A, B \in \mathrm{Lin}(\mathcal{H}) \to A \cdot B \in \mathrm{Lin}(\mathcal{H}).$$

  It is important to notice, though, that this operation is not internal in the set of Hermitian operators (i.e., those associated to physical magnitudes), since the product of two Hermitian operators is not Hermitian, in general.

- The anticommutator of two operators:

$$A, B \in \mathrm{Lin}(\mathcal{H}) \to [A, B]_+ \in \mathrm{Lin}(\mathcal{H}).$$

- The commutator of two operators:

$$A, B \in \mathrm{Lin}(\mathcal{H}) \to i[A, B] \in \mathrm{Lin}(\mathcal{H}).$$

Notice that these last two operations are internal in the space of Hermitian operators. How do we translate these operations into the GQM scheme? If we take $f_A, f_B \in \mathcal{F}_s(M_Q)$,

- the anticommutator of two operators, becomes the symmetric bracket or Jordan product of the functions (see Ref. [42]):

$$[A, B]_+ \to f_{[A,B]_+} = \{f_A, f_B\}_+ \in \mathcal{F}_s(M_Q).$$

- The commutator of two operators, transkates into the Poisson bracket of the functions:

$$i[A, B] \to f_{i[A,B]} = \{f_A, f_B\} \in \mathcal{F}_s(M_Q).$$

We may conclude, therefore, that the operators and their algebraic structures are encoded in the set of functions with the brackets associated to the Hermitian product. Thus we see why it makes sense to consider only that specific type of functions: it is a choice which guarantees to maintain all the algebraic structures which are required in the quantum description.

Another important property of the set of operators of quantum mechanics is the corresponding spectral theory. In any quantum system, it is of the utmost importance to be able to find eigenvalues and eigenvectors. In GQM, these objects are considered in the following way: Let f_A be the function associated to the observable A. Then, if we consider $\psi \in S_Q$,

- the eigenvectors of the operator A coincide with the critical points of the function f_A, i.e., $df_A(\psi) = 0 \Rightarrow \psi$ is an eigenvector of A.

- The eigenvalue of A at the eigenvector ψ is the value that the function f_A takes at the critical point ψ.

We finalize this discussion on the observables by noting that the identity operator $\mathbb{I}$ corresponds with the function

$$f_{\mathbb{I}}(q, p) = \sum_k \left(q_k^2 + p_k^2 \right), \tag{30}$$

and the Hamiltonian vector field of this function is precisely the generator of phase transformations:

$$\{f_{\mathbb{I}}, \cdot\} = \sum_k \left(p_k \frac{\partial}{\partial q_k} - q_k \frac{\partial}{\partial p_k} \right) = \Gamma. \tag{31}$$

4.4. The dynamics

As in the classical case, the dynamics can be implemented in different forms, always in a way which is compatible with the geometric structures introduced so far:

- In the Schrödinger picture, the dynamics is described as the integral curves of the vector field X_{f_H}, where H is the Hamiltonian operator of the system:

$$X_{f_H} = \hbar^{-1}\{f_H, \cdot\}. \tag{32}$$

- In the Heisenberg picture, the dynamics is introduced by transferring the Heisenberg equation into the language of functions:

$$\dot{f}_A = \hbar^{-1}\{f_H, f_A\}. \tag{33}$$

For example, the von Neumann equation is rewritten as:

$$\dot{f}_\rho = \hbar^{-1}\{f_H, f_\rho\}, \tag{34}$$

where f_ρ is the function associated to the density matrix.

Therefore, it is possible to describe quantum dynamics as a flow of a vector field on the manifold M_Q or on the set of quadratic functions of the manifold. Such a vector field is a Hamiltonian vector field with respect to the Poisson bracket encoded in the Hermitian structure of the system.

The dynamics thus defined preserves the norm of the state, which allows us to restrict the set of admissible states to those with norm equal to one. This can be proven by analyzing the evolution of the function $f_{\mathbb{I}}$, given by the Poisson bracket with the Hamiltonian:

$$\dot{f}_{\mathbb{I}} = \hbar^{-1}\{f_H, f_{\mathbb{I}}\}. \tag{35}$$

But because of the properties of the bracket, $\{f_H, f_{\mathbb{I}}\} = f_{[H,\mathbb{I}]} = 0$, and thus the flow is restricted to the sphere S_Q.

Example 1 *Let us consider a simple two-level quantum system, defined on $\mathbb{C}^2$. As a real manifold, $M_Q \sim \mathbb{R}^4$. Consider then a Hamiltonian $H : \mathbb{C}^2 \to \mathbb{C}^2$:*

$$H = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix}. \tag{36}$$

If we consider it as a matrix on the real vector space M_Q, it reads:

$$H_{\mathbb{R}} = \begin{bmatrix} H_{q_1 q_1} & H_{q_1 p_1} & H_{q_1 q_2} & H_{q_1 p_2} \\ H_{p_1 q_1} & H_{p_1 p_1} & H_{p_1 q_2} & H_{p_1 p_2} \\ H_{q_2 q_1} & H_{q_2 p_1} & H_{q_2 q_2} & H_{q_2 p_2} \\ H_{p_2 q_1} & H_{p_2 p_1} & H_{p_2 q_2} & H_{p_2 p_2} \end{bmatrix}. \tag{37}$$

It is easy to prove that this matrix is symmetric if the Hamiltonian is Hermitian ($H_{12} = H_{21}^*$).

The function f_H in $\mathcal{F}_s(M_Q)$ becomes thus:

$$f_H = \psi_{\mathbb{R}}^t H_{\mathbb{R}} \psi_{\mathbb{R}}, \quad \text{where} \quad \psi_{\mathbb{R}} = (q_1, p_1, q_2, p_2)^t$$

and then, the Hamiltonian vector field turns out to be:

$$X_H = \hbar^{-1} \left(\frac{\partial f_H}{\partial p_1} \frac{\partial}{\partial q_1} - \frac{\partial f_H}{\partial q_1} \frac{\partial}{\partial p_1} + \frac{\partial f_H}{\partial p_2} \frac{\partial}{\partial q_2} - \frac{\partial f_H}{\partial q_2} \frac{\partial}{\partial p_2} \right)$$

and its integral curves are precisely the expression of Schrödinger equation when we write it back in complex terms:

$$\begin{aligned}
\dot{q}_1 &= \hbar^{-1}(H_{p_1 q_1} q_1 + H_{p_1 q_2} q_2 + H_{p_1 p_1} p_1 + H_{p_1 p_2} p_2), \\
\dot{p}_1 &= -\hbar^{-1}(H_{q_1 q_1} q_1 + H_{q_1 q_2} q_2 + H_{q_1 p_1} p_1 + H_{q_1 p_2} p_2), \\
\dot{q}_2 &= \hbar^{-1}(H_{p_2 q_2} q_2 + H_{p_2 q_1} q_1 + H_{p_2 p_2} p_2 + H_{p_2 p_1} p_1), \\
\dot{p}_2 &= -\hbar^{-1}(H_{q_2 q_2} q_2 + H_{q_2 q_1} q_1 + H_{q_2 p_2} p_2 + H_{q_2 p_1} p_1).
\end{aligned}$$

We can write these equations as:

$$\dot{\psi}_{\mathbb{R}} = -\hbar^{-1} \mathbf{J} H_{\mathbb{R}} \psi_{\mathbb{R}}, \quad \text{with} \quad \mathbf{J} = \begin{bmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \tag{38}$$

or, equivalently,

$$|\dot{\psi}\rangle = -\hbar^{-1} i H |\psi\rangle, \quad \text{where} \quad |\psi\rangle = \begin{bmatrix} q_1 + i p_1 \\ q_2 + i p_2 \end{bmatrix} \tag{39}$$

is the complex state vector in terms of the real coordinates. The operator $\mathbf{J}$, that satisfies $\mathbf{J}^2 = -I$, is called the complex structure. As it is apparent when comparing (38) and (39), it implements the multiplication by the imaginary unity i in the real presentation of the Hilbert space. Observe that $\mathbf{J}$ and $H_{\mathbb{R}}$ commute, this is due to the fact that the latter comes from an operator H in the complex Hilbert space.

5. Ehrenfest dynamics as a Hamiltonian system

In this section we show how to put together the dynamics of a quantum and a classical system following the presentation of the two previous sections. We are describing thus a physical system characterized by the following elements:

5.1. The set of states of our system

- First, let $\mathcal{H}$ be a Hilbert space which describes the quantum degrees of freedom of our system. For example, it could describe the electronic subsystem; in this case, it is the vector space corresponding to the completely antisymmetric representation of the permutation group S_N (i.e., a set of Slater determinants), where N is the number of electrons of the system and each electron lives in a Hilbert space of dimension M. Thus, the dimension of $\mathcal{H}$ will be $N_Q = \frac{M!}{N!(M-N)!}$.
  We know that it is a complex vector space, but we prefer to consider it as a real vector space with the double of degrees of freedom and denote it as M_Q. Also, in correspondence with the Hilbert space vectors in the usual formalism of quantum mechanics, several states in M_Q represent the same physical state. To consider true physical states one should extract only those corresponding to the projective space, which can be identified with a submanifold of M_Q. A more general approach is to consider the sphere of states with norm equal to one, S_Q, and take into account the phase transformations generated by Eq (25) in a proper way. We will discuss this in the following sections.
- Second, let M_C be a differentiable manifold which contains the classical degrees of freedom. We shall assume it to be a phase space, and thus it will have an even number of degrees of freedom and it shall be endowed with a non degenerate Poisson bracket that in Darboux cordinates $(\vec{R}, \vec{P})$ reads

$$\{f, g\}_C = \sum_J \frac{\partial f}{\partial P_J} \frac{\partial g}{\partial R_J} - \frac{\partial f}{\partial R_J} \frac{\partial g}{\partial P_J}.$$

- Third, we let our state space $\mathcal{S}$ be the Cartesian product of both manifolds,

$$\mathcal{S} := M_C \times M_Q.$$

Such a description has important implications: it is possible to consider each subsystem separately in a proper way but it is not possible to entangle the subsystems with one another. As long as Ehrenfest dynamics disregards this possibility, the choice of the Cartesian product is the most natural one.

The coordinates that describe the state of the system are:

- The positions and momenta of the nuclei:

$$(\vec{R}, \vec{P}) \in M_C. \tag{40}$$

We will have $3N_C + 3N_C$ of these, for N_C the number of nuclei of the system.

- The real and imaginary parts of the coordinates of the Hilbert space vectors with respect to some basis:

$$(\vec{q}, \vec{p}) \in M_Q. \tag{41}$$

We will have $N_Q + N_Q$ of these, for N_Q the complex dimension of the Hilbert space $\mathcal{H}$.

5.2. The observables

Our observables are functions defined on the state space $S = M_C \times M_Q$. We know from our discussion in the case of a purely quantum system that any function of the form (29) produces an evolution, via the Poisson bracket, which preserves the norm. In the MQCD case, we can easily write the analogue of the vector field (25) by writting:

$$\Gamma_Q = \mathbb{I} \otimes \Gamma. \tag{42}$$

This is again the infinitesimal generator of phase transformations for the quantum subsystem, but written at the level of the global state space $M_C \times M_Q$. A reasonable property to be asked to the functions chosen to represent our observables is to be constant under this transformation. From a mathematical point of view, we shall define the set of possible observables, $\mathcal{O}$, as the set of all C^∞–functions on the set $M_C \times M_Q$ which are constant under phase changes on the quantum degrees of freedom, i.e.,

$$\mathcal{O} := \{ f \in C^\infty(M_C \times M_Q) | \ \Gamma_Q f = 0 \}. \tag{43}$$

As we shall see later, this choice reflects the fact that, when considered coupled together, the nonlinearity of classical mechanics expands also to MQCD. There are some important subsets that should be considered:

- The set of classical functions: these are functions which depend only on the classical degrees of freedom. Mathematically, they can be written as those functions $f \in \mathcal{O}$ such that there exists a function $f_C \in C^\infty(M_C)$ such that

$$f(\vec{R}, \vec{P}, \vec{q}, \vec{p}) = f_C(\vec{R}, \vec{P})\,.$$

We denote this subset as $\mathcal{O}_C$. An example of a function belonging to this set is the linear momentum of the nuclei.

- The set of **generalized quantum functions**: functions which depend only on the quantum degrees of freedom and which are constant under changes in the global phase. Mathematically, they can be written as those functions $f \in \mathcal{O}$ such that there exists a function $f_Q \in C^\infty(M_Q)$ such that

$$f(\vec{R}, \vec{P}, \vec{q}, \vec{p}) = f_Q(\vec{q}, \vec{p}); \quad \Gamma(f_Q) = 0\,. \tag{44}$$

We denote these functions as $\mathcal{O}_Q$. We have added the adjective "generalized" because this set is too large to represent only the set of pure quantum observables. These later functions, should be considered, when necessary, as a smaller subset, which corresponds to the set of functions defined in Eq. (29). We denote this

smaller subset as $\mathcal{O}_Q^s$. An example of a function belonging to $\mathcal{O}_Q^s$ is the linear momentum of the electrons.

- A third interesting subset is the set of arbitrary linear combinations of the subsets above, i.e., those functions which are written as the sum of a purely classical function and a purely quantum one:

$$f(\vec{R}, \vec{P}, \vec{q}, \vec{p}) = f_C(\vec{R}, \vec{P}) + f_Q(\vec{q}, \vec{p}). \tag{45}$$

We will denote this set as $\mathcal{O}_{C+Q}$. An element of this set of functions is the total linear momentum of the composed system.

We would like to make a final but very important remark. We have not chosen the set of observables as

$$\mathcal{P} := \left\{ f_A \in C^\infty(M_C \times M_Q) | f_A = \langle \psi | A(\vec{R}, \vec{P}) \psi \rangle \right\}, \tag{46}$$

for $A(\vec{R}, \vec{P})$ a linear operator on the Hilbert space $\mathcal{H}$ depending on the classical degrees of freedom because of two reasons:

- It is evident that the set above is a subset of (43) and thus we are not loosing any of these observables. But it is a well known property that Ehrenfest dynamics is not linear it does not preserve $\mathcal{P}$. We must thus enlarge the set (46).

- We are going to introduce in the next section a Poisson bracket on the space of observables. For that bracket to close a Poisson algebra, we need to consider the whole set (43).

It is important to notice that in the set (43) there are operators which are not representing linear operators for the quantum part of the system and hence the set of properties listed in Section 4 for the pure quantum case are meaningless for them. But this is a natural feature of the dynamics we are considering, because of its nonlinear nature.

5.3. Geometry and the Poisson bracket on the classical-quantum world

As we assume that both the classical and the quantum subsystems are endowed with Poisson brackets, we face the same problem we have when combining, from a classical mechanics perspective, two classical systems. Therefore it is immediate to conclude that the corresponding Poisson structures can be combined as:

$$\{\cdot, \cdot\} := \{\cdot, \cdot\}_C + \hbar^{-1}\{\cdot, \cdot\}_Q, \tag{47}$$

where the term $\{\cdot, \cdot\}_C$ acts on the degrees of freedom of the first manifold and $\{\cdot, \cdot\}_Q$ acts on the degrees of freedom of the second one. It is a known fact [41] that such a superposition of Poisson brackets always produces a well defined Poisson structure in the product space.

The set of pure classical functions $\mathcal{O}_C$ and the set of quantum generalized functions $\mathcal{O}_Q$ are closed under the Poisson bracket. The same happens with the quantum functions $\mathcal{O}_Q^s$ and the set of linear combinations $\mathcal{O}_{C+Q}$. In mathematical terms, what we have is

a family of Poisson subalgebras. This property ensures that the description of purely classical or purely quantum systems, or even both systems at once but uncoupled to each other, can be done within the formalism.

Once the Poisson bracket on $M_C \times M_Q$ has been introduced, one can prove, in analogy to the full quantum case, that the infinitesimal generator of the phase transformations is the Hamiltonian vector field of the identity operator, $\Gamma_Q = \{f_{\mathbb{I}}, \cdot\}$. Therefore, a function is a legitimate observable if it commutes with $f_{\mathbb{I}}$: $\{f_{\mathbb{I}}, f\} = 0$.

5.4. The definition of the dynamics

Analogously to the description given in Sections 3 and 4, the dynamics of the mixed quantum classical systems can be implemented on

- The manifold which represents the set of states by defining a vector field whose integral curves represent the solutions of the dynamics (Schrödinger picture).

- The set of functions (please note the differences between the classical and the quantum cases) defined on the set of states which represent the set of observables of the system. In this case the Poisson bracket of the functions with the Hamiltonian of the system defines the corresponding evolution (Heisenberg picture).

Both approaches are not disconnected, since they can be easily related:

$$X_H = \{f_H, \cdot\}, \tag{48}$$

where we denote by X_H the vector field which represents the dynamics on the phase space and by f_H the function which corresponds to the Hamiltonian of the complete system.

We can now proceed to our first goal: to provide a Hamiltonian description of Ehrenfest dynamics in terms of a Poisson structure. We thus define the following Hamiltonian system:

- A state space corresponding to the Cartesian product $M_C \times M_Q$.

- A set of operators corresponding to the set of functions $\mathcal{O}$ defined in Eq. (43).

- The Poisson bracket defined in Eq. (47).

- And finally, the dynamics introduced by the following Hamiltonian function:

$$f_H(\vec{R}, \vec{P}, \vec{q}, \vec{p}) := \sum_J \frac{\vec{P}_J^2}{2M_J} + \langle \psi(\vec{q}, \vec{p}) | H_e(\vec{R}) \psi(\vec{q}, \vec{p}) \rangle, \tag{49}$$

where H_e is the expression of the electronic Hamiltonian, M_J are the masses of the classical subsystem of the nuclei and $\psi(\vec{q}, \vec{p})$ is the real-space representation of the state ψ analogous to $|\psi\rangle$ in Eq. (39).

As a result, the dynamics of both subsystems are obtained easily. In the Schrödinger picture we obtain:

$$\dot{\vec{R}} = \frac{\partial f_H}{\partial \vec{P}} = M^{-1}\vec{P}, \tag{50}$$

$$\dot{\vec{P}} = -\frac{\partial f_H}{\partial \vec{R}} = -\text{grad}(\langle \psi(\vec{q}, \vec{p}) | H_e(\vec{R}) \psi(\vec{q}, \vec{p}) \rangle), \tag{51}$$

$$\dot{q}_k = \hbar^{-1} \frac{\partial f_H}{\partial p_k}, \quad k = 1, \dots, N_Q, \tag{52}$$

$$\dot{p}_k = -\hbar^{-1} \frac{\partial f_H}{\partial q_k}, \quad k = 1, \dots, N_Q. \tag{53}$$

This set of equations corresponds exactly with Ehrenfest dynamics.

Finally, it is important to verify that the dynamics preserves the set of observables $\mathcal{O}$, i.e., for any observable f, $\{f_H, f\} \in \mathcal{O}$. This can be easily proven since we have established that an observable belongs to $\mathcal{O}$ if it Poisson-commutes with $f_{\mathbb{I}}$. Thus, as $f_H \in \mathcal{O}$, if we consider an observable $f \in \mathcal{O}$, by the Jacobi identity:

$$\{f_{\mathbb{I}}, \{f_H, f\}\} = -\{f, \{f_{\mathbb{I}}, f_H\}\} - \{f_H, \{f, f_{\mathbb{I}}\}\} = 0. \tag{54}$$

6. A phase space description of the statistics of the Ehrenfest dynamics

The next step in our work is the definition of a statistical system associated to the dynamics we introduced above. The first ingredient for that is the definition of the distributions we shall be describing the system with.

The main conclusion from the previous section is that Ehrenfest dynamics can be described as a Hamiltonian system on a Poisson manifold. Therefore, we are in a situation similar to a standard classical system. We have seen that the dynamics preserves the submanifold $M_C \times S_Q$ (S_Q being the sphere in Eq. (26)), and thus it is natural to consider such a manifold as the space of our statistical system.

We have thus to construct now a statistical system composed of two subsystems. We may think in introducing a total distribution factorizing as the product of a classical and a quantum distribution. But as the events of the classical and the quantum regimes are not independent, the two probabilities must be combined and not defined through two factorizing functions.

Hence we shall consider a density $F_{QC} \in \mathcal{O}$ and the canonical volume element $d\mu_{QC}$ in the quantum-classical phase space, restricted to $M_C \times S_Q$:

$$d\mu_{QC} := d\mu_C d\Omega_Q \,, \tag{55}$$

which allows to define the macrosopic average for any observable $M \in \mathcal{O}$:

$$\langle M \rangle := \int_{M_C \times S_Q} M(\vec{R}, \vec{P}, \vec{q}, \vec{p}) F_{QC}(\vec{R}, \vec{P}, \vec{q}, \vec{p}) d\mu_{QC}. \tag{56}$$

In the rest of the section we shall discuss in more detail the ingredients of this definition.

We start by the volume form. Given the classical phase space M_C with Darboux coordinates $(\vec{R}, \vec{P})$ (they always exist locally [41]) we define the volume element in the classical phase space by

$$d\mu_C := \prod_J dP_J dR_J, \tag{57}$$

which, as it is well known, is invariant under any purely classical Hamiltonian evolution, and does not depend on the choice of coordinates.

We might proceed in the same way for the quantum part of our system. Indeed, as we have written the quantum dynamics like a classical Hamiltonian one we could use the canonical invariant volume element describe in the previous paragraph $d\mu_Q$ on M_Q. However, new complications appear in this case as in the quantum part of the phase space we restrict the integration to S_Q and then we look for an invariant volume form in the unit sphere, rather than in the full Hilbert space.

The new ingredient that makes the restriction possible is the fact that all our observables and of course, also the Hamiltonian, are killed by Γ. This implies, as discussed before, that $f_{\mathbb{I}}$ is a constant of motion. Using this we decompose

$$d\mu_Q = df_{\mathbb{I}} d\widetilde{\Omega}_Q, \tag{58}$$

which is possible on $\mathcal{H} \setminus \{0\}$. The decomposition is not unique, but the restriction (pullback) of $d\widetilde{\Omega}_Q$ to the unit sphere gives a uniquely defined, invariant volume form on S_Q that we will denote by $d\Omega_Q$. The decomposition is nothing but the factorization into the radial part and the solid angle volume element.

Example 2 *For the simple case we studied above, where $\mathcal{H} = \mathbb{C}^2$ and hence $M_Q = \mathbb{R}^4$ and S_Q is a three dimensional sphere, the volume element above would be:*

$$d\Omega_Q = q_1 dq_2 dp_1 dp_2 - q_2 dq_1 dp_1 dp_2 + p_1 dq_1 dq_2 dp_2 - p_2 dq_1 dq_2 dp_1. \tag{59}$$

Now, we finally put together the two ingredients to obtain the invariant volume element $d\mu_{QC}$ in eq. (55).

We discuss now the properties we must require from F_{QC} in order for Eq. (56) to correcly define the statistical mechanics for the Ehrenfest dynamics.

- The expected value of the constant observable should be that constant, which implies that the integral on the whole set of states is equal to one:

$$\int_{M_C \times S_Q} F_{QC} d\mu_{QC} = 1. \tag{60}$$

- The average, for any observable f_A of the form (46) associated to a positive definite hermitian operator A should be positive. This implies the usual requirements of positive probability density in purely classical statistical mechanics.

It is simple to go from this phase space description to the formulation of a density operator ρ for the quantum system and make the construction closer to the usual description of Quantum Statistical Mechanics. The density operator is defined as follows:

$$\rho(\vec{R}, \vec{P}) := \int_{S_Q} d\mu_Q(\vec{q}, \vec{p}) F_{QC}(\vec{R}, \vec{P}, \vec{q}, \vec{p}) |\psi(\vec{q}, \vec{p})\rangle\langle\psi(\vec{q}, \vec{p})|, \tag{61}$$

where $|\psi(\vec{q}, \vec{p})\rangle\langle\psi(\vec{q}, \vec{p})|$ is the projector on the quantum state parametrized by the pair $(\vec{q}, \vec{p})$. The average value of a pure quantum magnitude A, represented by the quadratic funtion f_A can be computed as:

$$\langle A \rangle(\vec{R}, \vec{P}) := \text{Tr}(\rho(\vec{R}, \vec{P})A) = \int_{S_Q} d\mu_Q(\vec{q}, \vec{p}) F_{QC}(\vec{R}, \vec{P}, \vec{q}, \vec{p}) f_A(\vec{q}, \vec{p}). \tag{62}$$

To obtain the corresponding total average, it is required to integrate the resulting object on the classical phase space:

$$\langle A \rangle := \int_{M_C} d\mu_C(\vec{R}, \vec{P}) \langle A \rangle (\vec{R}, \vec{P}). \tag{63}$$

So far we have discussed general considerations about the statistical mechanics of our system. Now we should include the dynamics in the game. Given that we have formulated the Ehrenfest dynamics as a Hamiltonian system, it is well known [37] which is the evolution of the density function F_{QC}. It is given by the **Liouville equation**

$$\frac{dF_{QC}}{dt} + \{f_H, F_{QC}\} = 0, \tag{64}$$

where, in the derivation of the equation, it is an essential requirement the invariance of the volume form under the evolution of the system.

The equilibrium statistical mechanics is obtained by requiring $\dot{F}_{QC} = 0$, which making use of (64) is equivalent to

$$\{f_H, F_{QC}\} = 0,$$

or, in other words, F_{QC} should be a constant of motion. An obvious non trivial constant of motion is given by any function of f_H. The question is if there are more. To answer this we should examine closely our particular dynamics. In several occasions we have mentioned the non linear character of a generic Ehrenfest system. This is an essential ingredient, because due to this fact we do not expect any other constant of motion that a function of the Hamiltonian itself. This is in contrast with the case of linear equations of motion, where the system is necessarily integrable.

The question of the existence of more constants of motion and, therefore, more candidates for the equilibrium density F_{QC} can be elucidated with a simple example that we discuss below. In it we show the presence of ergodic regions (open regions in the leave of constant energy densely covered by a single orbit). This rules out the existence of constants of motion different from the constant function in the region (i.e., functions of f_H).

Example 3 *In the following example we will study a simple toy model in which the coupling between classical and quantum degrees of freedom gives rise to chaotic behavior and the appeerence of ergodic regions.*

The system consists of a complex two dimensional Hilbert space $M_Q = \mathbb{C}^2$ and a classical 2-D phase space where we define a 1-D harmonic oscillator. Using coordinates (I_θ, θ) for the classical variables (action-angle coordinates for the oscillator) and $\Psi \in \mathbb{C}^2$ we define the following Hamiltonian

$$f_H = I_\theta + \frac{1}{2} \langle \Psi | \sigma_z + \epsilon \cos(\theta) \sigma_x | \Psi \rangle,$$

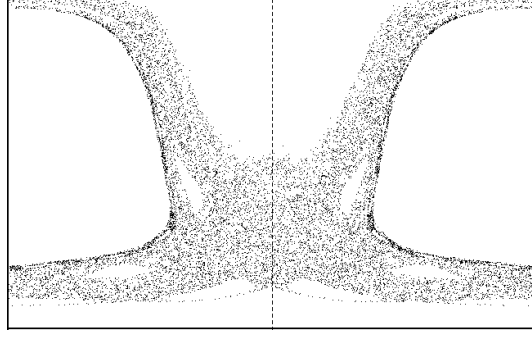*with σ_x, σ_z the Pauli sigma matrices.*

Figure 1. The plot shows a single orbit of the Poincaré map of Eq. (66) at $\theta = 0$. The angle $\phi \in [-\pi, \pi]$ is plotted in the horizontal axis and $I_\phi \in [0, 1]$ in the vertical one. We have taken $\epsilon = 0.8$. The energy determines I_θ and its actual value does not affect the dynamics of ϕ and I_ϕ.

We parametrize the normalized quantum state by

$$|\Psi\rangle = e^{i\alpha} \left[\begin{array}{c} I_\phi \\ e^{i\phi}\sqrt{1 - I_\phi^2} \end{array} \right]. \tag{65}$$

One can now easily check that I_ϕ and ϕ are canonical conjugate variables. In these variables the Hamiltonian reads

$$f_H = I_\theta + I_\phi^2 + \epsilon I_\phi \sqrt{1 - I_\phi^2} \cos(\theta) \cos(\phi), \tag{66}$$

where ϵ measures the coupling of the classical and quantum systems.

In the limit of vanishing ϵ the system is integrable and actually linear in these coordinates. However for non vanishing ϵ the model becomes non linear and, as we will show below, regions of chaotic motion emerge.

In order to understand the behaviour of our system it is useful to study its Poincaré map (see Ref. [41] for the definition). To this end we take the transversal (or Poincaré) section at $\theta = 0$ and, taking into account the conservation of energy, only two coordinates are needed to describe the map, we have chosen the quantum variables I_ϕ and ϕ.‡

By examining the plot of Fig. 1, one sees that the orbit densely fills a large region of the Poincaré section and therefore any constant of motion should be the constant function in that region. In the presence of such an ergodic evolution the only constants of motion are functions of the Hamiltonian.

As a consequence we can claim that, generically within the Ehrenfest dynamics, the only functions which commute with the Hamiltonian in (64) are those which are function of the Hamiltonian f_H itself. As the Poisson bracket is skew-symmetric, the

‡ In our construction of the Poincaré map we represent the value of ϕ and I_ϕ whenever the periodic coordinate θ takes the value $\theta = 0$. The successive values of ϕ and I_ϕ, for some initial condition, form our orbit. As stressed in [41] the Poincaré map is a very useful tool in the context of non linear dynamics as many properties of the full system like ergodicity, chaos or regular behaviour, may be inferred from the same property of the Poincaré map.

property follows trivially. Ergodicity helps us to assert, roughly speaking, that in general no other function in $\mathcal{O}$ will be a constant of the motion.

Thus, at this stage, we can finish our construction with the equilibrium distribution associated to Ehrenfest dynamics. Taking into account the ergodicity of the dynamics, we can impose the equal-probabilities condition to the configurations of an isolated Ehrenfest system, which leads to the microcanonical ensemble, (see Ref. [43]).

In the case in which this system is weakly coupled to a bath, if we assume that the dynamics of the system plus bath is ergodic as well, such that system plus bath are microcanonically distributed, then the statistics of the Ehrenfest system are given by the well known canonical probability density (see, for example, Refs. [37, 38, 44]):

$$F_{QC}^c(\vec{R}, \vec{P}, \vec{q}, \vec{p}) = Z^{-1} e^{-\beta f_H}, \qquad Z = \int_{M_C \times S_Q} e^{-\beta f_H} d\mu_{QC}, \tag{67}$$

where β^{-1}, proportional to the temperature of the subsystem, is the parameter governing the equilibrium between the system and the bath. An information-theoretic approach to the equiprobability in the microcanonical ensemble and to Eq. (67) may be seen in Ref. [45] or in Refs. [46, 47] for a much more modern and mathematically sound exposition. We also strongly recommend the recent work of P. Reimann [48, 49] for a foundation of Statistical Mechanics under experimentally realistic conditions.

7. Application: Nosé formalism for Ehrenfest systems

We now procced to extend the non-stochastic method proposed by Nosé [17, 18] to our Hamiltonian (49). Consider a system defined on $M_C \times M_Q$ as before and an extension of that system including two new classical degrees of freedom (s, p_s), what produces a total state space

$$M_C \times M_Q \times \mathbb{R}^2.$$

In this case, in order to include the quantum degrees of freedom, we must take into account the problem of the deformation of the domain (see the change of coordinates of Eq. (77)) of integration we dealt with in the previous section. Thus we must rewrite the Hamiltonian given in Eq. (49) in order to extend the domain of the quantum part from the sphere to the whole M_Q. In order to do this, we consider:

$$H(\vec{R}, \vec{P}, \vec{q}, \vec{p}) := \sum_k \frac{\vec{P}_k^2}{2M} + \frac{\langle \psi(\vec{q}, \vec{p}) | H^e(\vec{R}) \psi(\vec{q}, \vec{p}) \rangle}{\langle \psi(\vec{q}, \vec{p}) | \psi(\vec{q}, \vec{p}) \rangle}$$
$$=: H^N(\vec{P}) + e_{H^e}(\vec{q}, \vec{p}, \vec{R}), \tag{68}$$

Now we transform this Hamiltonian into the "extended" one, by introducing a dependence with respect to the new degrees of freedom:

$$H(\vec{R}, \vec{P}, \vec{q}, \vec{p}, s, p_s) := H^N(\vec{P}/s) + e_{H^e}(\vec{q}, \vec{p}/s, \vec{R}) + \frac{p_s^2}{2Q} + gkT \log(s). \tag{69}$$

This is very similar to the method proposed by Nosé [17, 18] for thermostating classical systems. The Nosé technique is basically an algorithm to produce the

correct equilibrium distribution and, therefore, the interpretation of the coordinate s as describing the behaviour of some 'thermostat' is only metaphorical. In the same sense, the particular form of the last two terms in the above Hamiltonian is just the one needed for the theorem that we mention in the following lines to work.

The extended equations of motion read now:

$$\dot{\vec{R}} = \vec{P}/(Ms^2), \tag{70}$$

$$\dot{\vec{P}} = -\mathrm{grad}_{\vec{R}}\left(e_{H^e}(\vec{q}, \vec{p}/s, \vec{R})\right), \tag{71}$$

$$\dot{q}_k = \frac{\hbar^{-1}s^{-1}}{\langle\psi|\psi\rangle}(H_{p_k q_1}q_1 + \ldots + H_{p_k p_{N_Q}}p_{N_Q}/s - e_{H^e}(\vec{q}, \vec{p}/s, \vec{R})p_k), \tag{72}$$

$$\dot{p}_k = -\frac{\hbar^{-1}}{\langle\psi|\psi\rangle}(H_{q_k q_1}q_1 + \ldots + H_{q_k p_{N_Q}}p_{N_Q}/s - e_{H^e}(\vec{q}, \vec{p}/s, \vec{R})q_k), \tag{73}$$

$$\dot{s} = \frac{p_s}{Q}, \tag{74}$$

$$\dot{p}_s = s^{-1}\sum_k \dot{q}^k + \sum_j \dot{R}^j - s^{-1}gKT, \tag{75}$$

where $k = 1, \ldots, N_Q$.

Now we generalize the standard result of Nosé [17, 18], by proving the equivalence of the microcanonical distribution of the extended system and the canonical distribution of the original one. The equations (70-75) are the necessary ones to implement the microcanonical scheme once we assume the ergodic hypothesis for the extended system. To prove the equivalence with the canonical distribution of the original system, we take the Hamiltonian above, and we consider the corresponding microcanonical distribution:

$$Z = \int_{M_C \times M_Q \times \mathbb{R}^2} d\mu_C d\mu_Q dp_s ds\, \delta(H(\vec{R}, \vec{P}, \vec{q}, \vec{p}, s, p_s) - E), \tag{76}$$

where $d\mu_C d\mu_Q$ is the volume element on $M_C \times M_Q$.

If we consider the following noncanonical transformation on $M_C \times M_Q \times \mathbb{R}^2$:

$$R'^j = R^j, \quad P'_j = \frac{P_j}{s}, \quad q'^k = q^k, \quad p'_k = \frac{p_k}{s}, \quad s' = s, \quad p'_s = p_s, \tag{77}$$

the partition function reads (we use the same symbol again for the transformed variables but include the jacobian which is equal to s^D):

$$Z = \int_{M_C \times M_Q \times \mathbb{R}^2} d\mu_C d\mu_Q dp_s ds\, s^D$$
$$\delta\left(H^N(\vec{P}) + e_{H^e}(\vec{q}, \vec{p}, \vec{R}) + \frac{p_s^2}{2Q} + gkT\log(s) - E\right), \tag{78}$$

where D is the number of degrees of freedom of the system (the sum of classical and quantum degrees of freedom).

As the original integral domain includes the complete M_Q, and therefore a rescaling of momenta does not modify it, we can use the equivalence

$$\delta(f(s)) = \delta(s - s_0)/|f'(s_0)|,$$

where

$$s_0 = \exp\left(-\frac{H^N(\vec{P}) + e_{H^e}(\vec{q}, \vec{p}, \vec{R}) + \frac{p_s^2}{2Q} - E}{gkT}\right),$$

and write:

$$Z = \int_{M_C \times M_Q \times \mathbb{R}^2} d\mu_C d\mu_Q dp_S ds \; s^D$$

$$\delta\left[s - \exp\left(-\frac{H^N(\vec{P}) + e_{H^e}(\vec{q}, \vec{p}, \vec{R}) + \frac{p_s^2}{2Q} - E}{gkT}\right)\right]. \tag{79}$$

Integrating in the variable s, we get:

$$Z = \frac{1}{gkT} \int dp_s \exp\left[\frac{D+1}{gkT}\left(E - \frac{p_s^2}{2Q}\right)\right]$$

$$\int_{M_C \times M_Q} d\mu_C d\mu_Q \exp\left[-\frac{D+1}{gkT}(H^N(\vec{P}) + e_{H^e}(\vec{q}, \vec{p}, \vec{R})\right]. \tag{80}$$

Then if we choose $g = D+1$ the exponential takes the desired form. Besides, we can notice that when calculating the average of any function $M \in \mathcal{O}$ (where $\mathcal{O}$ corresponds to Eq. (43) and therefore M does not depend on the extended variables), the quantity:

$$\frac{1}{(D+1)kT} \int dp_s \exp\left[\frac{1}{kT}\left(E - \frac{p_s^2}{2Q}\right)\right]$$

factorizes. If we also assume that the function M does not depend either on the norm of the quantum state (as it is the case for the quantum observables) and we decompose the volume element $d\mu_Q$ as Eq. (58), the radial part of the quantum integral also factorizes and cancels the analogous term arising from the partition function.

Thus we can write

$$\langle M \rangle = 1/Z \int_{M_C \times M_Q \times \mathbb{R}^2} d\mu_C df_{\mathbb{I}} d\tilde{\Omega}_Q dp_s ds M(\vec{R}, \vec{P}, \vec{q}, \vec{p}) \delta(H(\vec{R}, \vec{P}, \vec{q}, \vec{p}, s, p_s) - E)$$

$$= 1/Z \left(\frac{1}{(D+1)kT} \int dp_s \exp\left[\frac{1}{kT}\left(E - \frac{p_s^2}{2Q}\right)\right] \int_{\mathbb{R}} df_{\mathbb{I}} \times\right.$$

$$\left. \int_{M_C \times S_Q} d\mu_C d\Omega_Q M(\vec{R}, \vec{P}, \vec{q}, \vec{p}) \exp\left[-\frac{1}{kT}\left(H^N(\vec{P}) + e_{H^e}(\vec{q}, \vec{p}, \vec{R})\right)\right]\right)$$

where

$$Z = \frac{1}{(D+1)kT} \int dp_s \exp\left[\frac{1}{kT}\left(E - \frac{p_s^2}{2Q}\right)\right] \int_{\mathbb{R}} df_{\mathbb{I}} \times$$

$$\int_{M_C \times S_Q} d\mu_C d\Omega_Q \exp\left[-\frac{1}{kT}\left(H^N(\vec{P}) + e_{H^e}(\vec{q}, \vec{p}, \vec{R})\right)\right].$$

Hence we have proved that the microcanonical distribution of the extended dynamical system created by Eq.(69) is equivalent to the canonical distribution created by the Hamiltonian

$$H(\vec{R}, \vec{P}, \vec{q}, \vec{p}) = H^N(\vec{P}) + e_{H^e}(\vec{q}, \vec{p}, \vec{R}).$$

8. Conclusions and future work

In this paper we have constructed a rigorous Hamiltonian description of the Ehrenfest dynamics of an isolated system by combining the Poisson brackets formulation of classical mechanics with the geometric formulation of quantum mechanics. We have also constructed the corresponding statistical description and obtained the associated Liouville equation. Finally, after verifying numerically that the Ehrenfest dynamics is ergodic, we justify the equilibrium distribution produced by it.

It is important to keep in mind the restriction to finite-dimensional quantum systems that we fixed as starting point, since our first goal is to apply our construction to Molecular Dynamics. From a theoretical point of view, though, it is very interesting to perform the same type of analysis for infinite dimensional quantum systems (note that the Ehrenfest dynamics as formulated in [4, 5] consists of classical nuclei and an infinite-dimensional Hilbert space for the electronic subsystem). Formally, the construction can be defined in the same way, once we adapt the language to infinite dimensional manifolds. But the nonlinearity of the resulting dynamics imposes very challenging problems at many levels, for instance at the very existence of the solutions of the Hamiltonian dynamical flow. Another interesting problem would be to recover, within the geometrical formalism, the classical-quantum system as a suitable classical limit for the nuclear degrees of freedom of an original completely quantum system (similarly to what is done in [4, 5] in the standard approach). We hope to address these problems in the future.

The definition of the Hamiltonian in Eq.(49) and its associated canonical equilibrium distribution Eq. (67) allows us now to use (classical) Monte Carlo methods for computing canonical equilibrium averages in our system, given by the expression Eq. (56). But this formalism also allows to easily introduce a Nosé extended system scheme to compute averages in the canonical ensemble by performing constant energy Molecular Dynamics simulations. This is a very important feature of the final setting, because the situations where the Ehrenfest approach is necessary (i.e. those where the electronic energy gap is small and the Born-Oppenheimer approximation is not sufficient) the effect of the temperature can be relevant. A method for the simulation of the canonical ensemble is thus of the greatest importance.

Alternatively, if we wish to perform MD simulations using stochastic methods, we should first construct the Langevin dynamics associated with our Hamiltonian Eq. (49) and equations Eqs. (50)-(53). To develop this program, we also need an analogue of the Fokker-Planck equation associated with those Langevin equations and then we have to check whether its solution at infinite time approaches Eq.(67). Presently we are working on this point [50], i.e., on the extension of our formalism to an associated stochastic MD.

Acknowledgments

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